

Silicon-ion-implanted PMMA with nanostructured ultrathin layers for plastic electronics

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Abstract. Being of interest for plastic electronics, ion-beam produced nanostructure, namely silicon ion (Si^+) implanted polymethyl-methacrylate (PMMA) with ultrathin nanostructured dielectric (NSD) top layer and nanocomposite (NC) buried layer, is examined by electric measurements. In the proposed field-effect organic nanomaterial structure produced within the PMMA network by ion implantation with low energy (50 keV) Si^+ at the fluence of $3.2 \times 10^{16} \text{ cm}^{-2}$, the gate NSD is ion-nanotracks-modified low-conductive surface layer, and the channel NC consists of carbon nanoclusters. In the studied ion-modified PMMA field-effect configuration, the gate NSD and the buried NC are formed as planar layers both with a thickness of about 80 nm. The NC channel of nano-clustered amorphous carbon (that is an organic semiconductor) provides a huge increase in the electrical conduction of the material in the subsurface region, but also modulates the electric field distribution in the drift region. The field effect via the gate NSD is analyzed. The most important performance parameters, such as the charge carrier field-effect mobility and amplification of this particular type of PMMA-based transconductance device with NC *n*-type channel and gate NSD top layer, are determined.

1. Introduction

The electrical properties of the ion-modified polymers are of great importance for their electronic applications [1-6]. In particular, the low-energy (keV range) ion irradiation and ion implantation have shown a significant enhancement of the electrical conductivity of normally insulating plastics, such as poly-(methyl methacrylate) (PMMA), very interesting material for plastic electronics. The ion-beam sensitivity of PMMA makes it possible to considerably modify and engineer the electrical conductivity of this polymer [7, 8] that opens ways to use ion-implanted PMMA in flexible electronics, optoelectronics and in various high-tech and industry areas. Nowadays there is an increasing interest of fabrication of organic thin-film transistors (TFT) utilizing the electrical properties of ultrathin organic layers on the surface of ion-implanted polymers [9, 10]. Previous our investigations [11, 12] indicated that the implantation of bulk PMMA by silicon ions (Si^+) accelerated to a relatively low ion energy of 50 keV and at the fluence of $3.2 \times 10^{16} \text{ Si}^+/\text{cm}^2$ does result in the formation of carbonized ion-modified material close to the very surface within this plastic. In the present work, we report on the electrical response of an organic electronic element with simple configuration based on field effect in Si^+ -implanted PMMA, observed in a sandwich structure of the type *dielectric/semiconductor/*

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insulator created on the surface of PMMA by the same ion implantation. It is of scientific and technology interest to estimate the electrical parameters relevant to the performance of such a device based on ion-implanted polymer. We demonstrated that in the ion-beam produced nanostructure driven by a buried ion-implanted nanocomposite (NC) ultrathin layer (as a channel) and a gate nanostructured dielectric (NSD) ultrathin top layer, the field effect and the device functionality can be efficiently controlled.

2. Experimental

The sample was a plate of size $1\text{ cm} \times 1\text{ cm}$ from PMMA commercially available (Röhm Plexiglas) with a thickness of 5 mm. It was implanted with Si^+ ions at a relatively low energy of 50 keV and Si^+ ion fluence of $3.2 \times 10^{16}\text{ cm}^{-2}$. The experimental details have been described elsewhere [11].

For electrical measurements, the Si^+ -implanted PMMA sample was electroded with silver paste. Electric contacts (1 mm-narrow, 1 cm-long) from silver paste were deposited at two opposite edges of the implanted surface of the PMMA sample, as schematically shown in figure 1. Direct current (DC) measurements were conducted by Keithley 617 Programmable Electrometer controlled by computer. The DC transconductance of Si^+ -implanted PMMA was studied upon applying a gate voltage on a third (gate) electrode from copper (width $W = 1\text{ cm}$, length $L = 3\text{ mm}$) placed on the implanted PMMA surface between the drain and the source side-electrodes (figure 1).

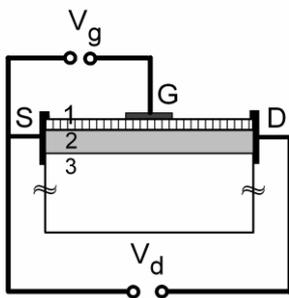


Figure 1. Schematic of the field-effect nanostructured Si^+ -implanted PMMA device with source (S), drain (D) and gate (G) electrodes. The spatial structure: (1) ion-nanotracks-modified low-conductive top layer, being a gate nanostructured dielectric (NSD); (2) conductive carbon nano-clustered ion-implanted nanocomposite (NC) buried layer; (3) the bulk of the non-implanted PMMA (the substrate from pristine PMMA).

In addition to the DC measurements, the electrical response of the Si^+ -implanted PMMA was also examined under alternating (AC) electric field. In this case, a sinusoidal voltage with amplitude of 1 V was applied and the field frequency was swept in the range from 1 Hz to 30 kHz. The sampling signal from a Stanford Research Systems SR830 DSP lock-in build-in generator was acquired by a computer that controls the frequency sweep. A reference sample of non-implanted PMMA (the same as the one used as a substrate for the ion-implanted sample) was also measured. These measurements consisted in determination of the frequency dependent current flowing through the samples when the electric field was longitudinally applied to the ion-implanted layer.

The measurements were carried out under ambient environment (in air and at room temperature).

3. Results and Discussion

As known, the modification of electrical properties of ion implanted materials is due to chemical and structural changes upon ion implantation [1-6]. In particular, for hydrocarbon polymers like PMMA, these changes include polymer decomposition, loss of hydrogen and hydrocarbons, outgassing of light fragments and densification of remaining material, chain scissions accompanying with formation of double bonds ($\text{C}=\text{C}$) where the side groups containing carbonyl groups are broken. As a result, a well defined subsurface layer from a more compacted material with carbonaceous structure having conjugated double bonds is formed [1-6] that actually leads to increased electrical conductivity even at low implantation fluence (of the order of $10^{14} - 10^{15}\text{ cm}^{-2}$) and relatively low ion energy (keV range).

In our case, the implantation of PMMA with 50 keV Si^+ ions at the fluence of $3.2 \times 10^{16}\text{ cm}^{-2}$ results in formation of nanostructured material within the PMMA substrate. Optical spectroscopy reveals the presence of carbonized material (namely hydrogenated amorphous carbon) with nano-

clustered structure (carbon nanoclusters, CNCs) in the ion-implanted region in the Si⁺-implanted PMMA [11, 13]. This carbonaceous structure has a three-dimensional network of independent clusters of *sp*² bonded carbon atoms. These rings fairly resemble the disordered graphite-like structures [1]. As a sensitive probe for local atomic bonding, Raman spectroscopy clearly evidences the nanometer-sized CNCs in the ion-implanted layer beneath the surface of Si⁺-implanted PMMA, and the polarized micro-Raman spectroscopy allows estimating even the orientation of the CNCs. The average size of the CNCs was estimated to be 3 – 5 nm [11, 13], and the material formed in the ion-implanted layer in Si⁺-implanted PMMA can be considered as nanocomposite (NC), i.e. CNCs within PMMA network.

Upon the conditions of the ion implantation we have performed, the 50 keV Si⁺ ions were implanted in PMMA in a very small depth (< 100 nm) beneath the surface, forming a buried planar NC layer of a thickness of about 80 nm under the surface [14] (figure 1). Further, by the present Si⁺-ion implantation a real doping of PMMA with silicon at a doping level of 1 – 2 at. %) is achieved in this ultrathin layer #2, as expected at the ion energy of 50 keV and the ion fluence higher than 10¹⁶ ions/cm² [15]. Si⁺-implanted PMMA becomes a typical organic semiconducting material [14].

The DC electrical response of the examined Si⁺-implanted PMMA is reported in figure 2(a). The linear current-voltage plot reveals Ohmic conductance of the formed NC layer that. This experimental fact is consistent with the electron hopping mechanism of conductivity [2-4, 16] (a variable range electron hopping conductivity through high-conducting CNCs separated by material with much lower conductivity, similarly to other examples of PMMA subjected to low-energy ion implantation [7, 9, 17]). From data in figure 2(a), the DC conductivity of the considered NC layer of Si⁺-implanted PMMA was calculated to be $\approx 6 \times 10^{-5}$ S/cm, much higher than that (< 10⁻¹⁵ S/cm) of the originally insulating PMMA substrate (the pristine PMMA, highly insulating plastic), i.e. an enhancement by more than ten orders of magnitude takes place as a result from ion implantation. Thus, at the implantation fluence of 3.2×10^{16} Si⁺/cm² Si⁺-implanted PMMA attains a DC conductivity typical for highly conductive amorphous phase of carbon and conducting polymers at room temperature [18].

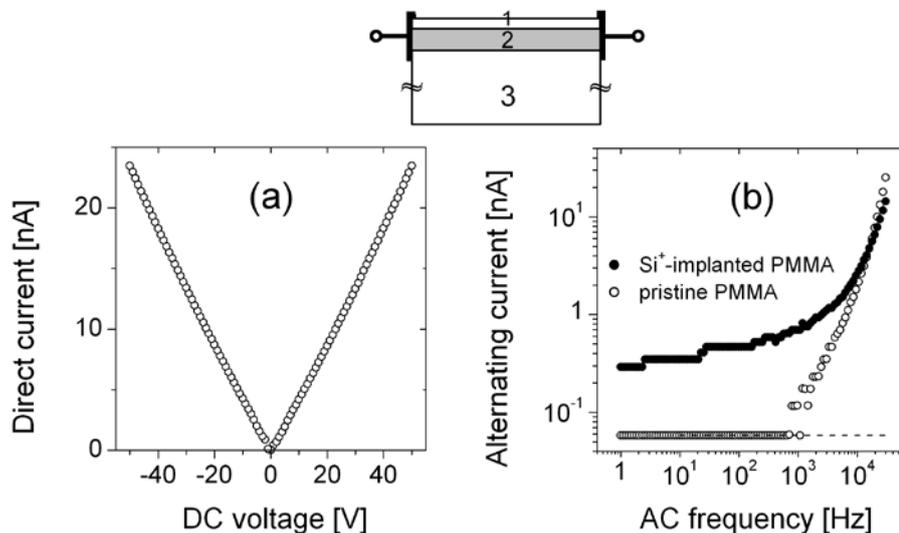


Figure 2. (a) DC current-voltage dependence in positive and negative voltage sweep (a) and AC frequency behavior (b) of Si⁺-implanted PMMA. For comparison, data for pristine PMMA is given in (b) (open circles). The dashed line indicates the sensitivity limit of the apparatus. At the top is schematically shown the measured structure with unconnected (floating) gate electrode.

The electrical response of the studied Si⁺-implanted PMMA was also characterized by AC measurements (figure 2(b)). They indicated that Si⁺ ion implantation of PMMA (in the present case at

an ion energy of 50 keV and at the fluence of $3.2 \times 10^{16} \text{ Si}^+/\text{cm}^2$) leads to a considerable enhancement of the AC conductivity of the NC layer, most pronounced at electric-field frequency below 1 kHz.

The spatial structure formed in the host PMMA by considered Si^+ -ion implantation consists of the following regions (in the depth) (recall figure 1): (i) ion-modified top layer (#1) with a thickness of about 80 – 100 nm [14]; (ii) a buried ion-implanted layer (#2) with a thickness of about 80 nm [14]; and (iii) the non-intact PMMA insulating bulk region (#3). Due to the ion-beam-produced nano-sized ion tracks along the trajectory of the impact ions (cylindrically-shaped tracks having nanoscale transversal dimension [1]) within the top ultrathin layer #1, the electronic and electrical properties of this ion-modified surface region differ from those of the pristine PMMA substrate (#3). Our complementary measurements of the leakage current through the gate in the examined electronic system (with the same electrode configuration) indicated a presence of an amount of free charge carriers (electrons) in the layer #1, i.e. it acts as a source of electrons. As such, the ion-tracks-modified surface layer #1 should be considered as a low-conductive (i.e. not ideal insulator) gate nanostructured dielectric (NSD), in contrast to the highly conductive ion-implanted NC layer #2 (actually, semiconducting *n*-type owing to the hydrogenated amorphous CNCs [19]). Due to the distribution of the ion-implanted material, both ion-modified ultrathin organic layers (the top NSD layer #1 and the buried NC layer #2) have diffusive interface with no sharp boundary between them.

Upon suitable conditions, the sandwich-like *dielectric/semiconductor/insulator* structure formed within the polymer PMMA allows a field-effect-transistor (FET)-like operation by the buried ultrathin NC layer #2 used as a channel of organic thin film FET. Thus, with an appropriate electrode configuration, both spatial structure and the formed organic nanomaterial in Si^+ -implanted PMMA enable the control of the channel current by a potential difference upon applying an external electric field (gate voltage). Our investigation has shown that by the above electrode geometry this complex organic structure exhibits a field-effect transconductance $\sim 0.35 \text{ nS}$, and thereby the ion-implanted material considered here is of practical interest for assembling of FET-like electronic elements.

Figure 3(a) reports output electrical characteristics of FET-like device based on the channel structure of the studied Si^+ -implanted PMMA with two side electrodes (source and drain) and a top electrode (gate) as shown in figure 1. The results for the dependence of the drain-to-source current I_D versus the drain-to-source voltage V_D are in accordance with the output characteristics that correspond to an *n*-channel with electron accumulation mode. The field effect was relatively weak, as seen also by the transfer characteristics of the studied Si^+ -implanted PMMA FET-like configuration (figure 3(b)).

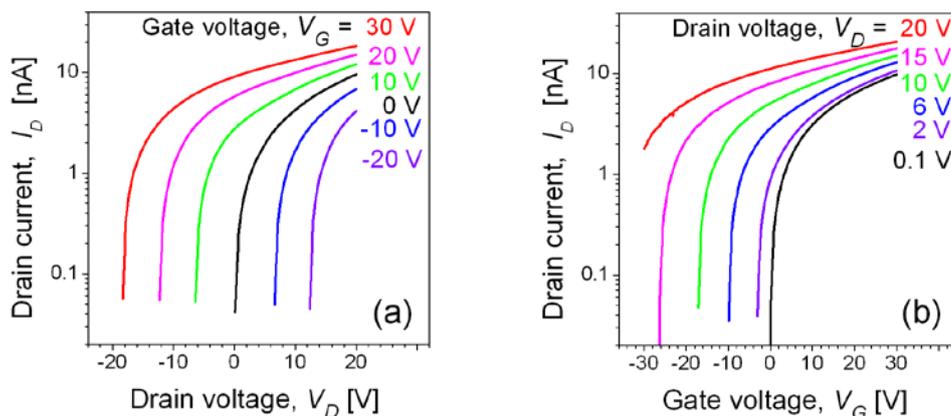


Figure 3. Output characteristics at various gate voltage V_G (a) and transfer characteristics at various drain voltage V_D (b) of the examined Si^+ -implanted PMMA transconductance device (schematically drawn in figure 1), all measured at room temperature.

The amplification taken from the transfer curve measured at $V_D = 0.1 \text{ V}$ as the maximum current on/off ratio obtained at fixed gate voltages 20 V and 0 V, was ≈ 300 . It should be noted that such a

value is much lower as compared to those reported for high-performance organic FETs [20, 21]. Further, the on/off ratio sharply decreases with the increasing drain-to-source voltage V_D (figure 4).

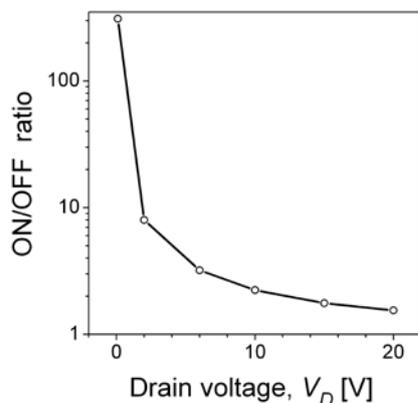


Figure 4. The maximum current on/off ratio obtained at fixed gate voltages 20 V and 0 V from the transfer characteristic curves of the examined Si⁺-implanted PMMA transconductance device at several values of the drain-to-source voltage V_D .

Using data from DC measurements, one can assess the effective mobility (μ) of the charge carriers relevant to the performance of the organic transconductance device. For the purpose, we have applied a procedure used for electrical characterization of TFTs [22], namely a differential method in a linear regime of transistor operation, i.e. at $V_{GS} \gg V_{DS}$. In our modeling, the curve measured at $V_D = 0.1$ V was chosen from the transfer characteristics family given in figure 3(b). We calculated $\mu \approx 0.02$ cm² V⁻¹ s⁻¹ (at room temperature, a result obtained by using the values $W = 1$ cm, $L = 3$ mm and $C_i = 40$ nF/cm², where W and L are the width and the length of the gate, respectively, and C_i is the capacitance per unit area of the NSD). Such a value of the charge carrier field-effect mobility in the considered Si⁺-implanted PMMA FET-like device is rather low as compared to the values (e.g., 1 – 5 cm² V⁻¹ s⁻¹) reported for the high-performance thin-film organic FETs [20, 21]. Reasonably, the device figures of merits strongly depend on the production implant process and on the device configuration.

4. Conclusions

Electrical properties of ion-implanted PMMA with ultrathin planar gate nanostructured dielectric (NSD) and nanocomposite (NC) buried layer are characterized, and a field-effect configuration is inspected as operated in such complex nanostructure of PMMA being implanted with low energy (50 keV) Si⁺ ions at the fluence of 3.2×10^{16} cm⁻². The electrical system of the all-organic transconductive device based on Si⁺-implanted PMMA examined here is driven through the formed NC ion-implanted layer (as a channel with a thickness of about 80 nm) of nano-clustered hydrogenated amorphous carbon as *n*-type organic semiconductor nanomaterial produced in PMMA by the ion implantation. The structure under study exhibits a feasible field effect which has a potential for electronic applications, e.g. in organic FET-like devices based on ion implantation-modified PMMA.

The formed field-effect organic structure and FET-like device on such layered nanomaterial may be of practical interest for plastic electronics and nano-electronics, in particular, for electrical sensing (e.g., charge-based sensing), as well as electrically-controlled bio-medical applications utilizing the high porosity, the nano-sized ion tracks within the NSD in the polymer, the bio-compatibility of PMMA (and ion-modified PMMA) and other useful properties of the ion-irradiated polymer surface and subsurface region.

The values of important electrical parameters, such as the charge carrier field-effect mobility and amplification of the considered type of polymer-based transconductance device appear to be accessible to optimization. The improving of the performance needs careful engineering (by the implant process) of the formed NC ion-implanted layer (channel) that is the most important, as well as the gate NSD. The implantation conditions (the ion energy and fluence, as well as the angle of incidence of the ion beam) determine the carbonaceous nanostructure and its in-depth distribution, and thereby, the in-depth electronic and electrical properties of the formed organic nanomaterial of both NSD and buried

NC layer, as well as the dielectric-semiconductor interface between them and its properties. These conditions are very important for the formation of an effective transconductance structure.

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